Next Generation Ambient Air Monitoring for Benzene and Toluene Compared with Traditional Methods at the Fenceline of an Indiana Oil Refinery

Motria Caudill[1], Wayne Whipple[1], Karen Oliver[2], Donald Whitaker[2]

[1]EPA Region 5, [2]EPA Office of Research and Development

Significance

- EPA's National Air Toxics Assessment (NATA)[1] shows benzene is one of the two top contributors to overall cancer risk in the U.S. from inhalation exposure.
- Toluene is a neurotoxin and an important tracer for mobile sources and industrial emissions.
- Air monitoring for VOCs is relatively expensive, because of required infrastructure and highly-skilled laboratory services.
- Highest benzene concentrations near industrial sites, most notably coke ovens & petroleum refineries.

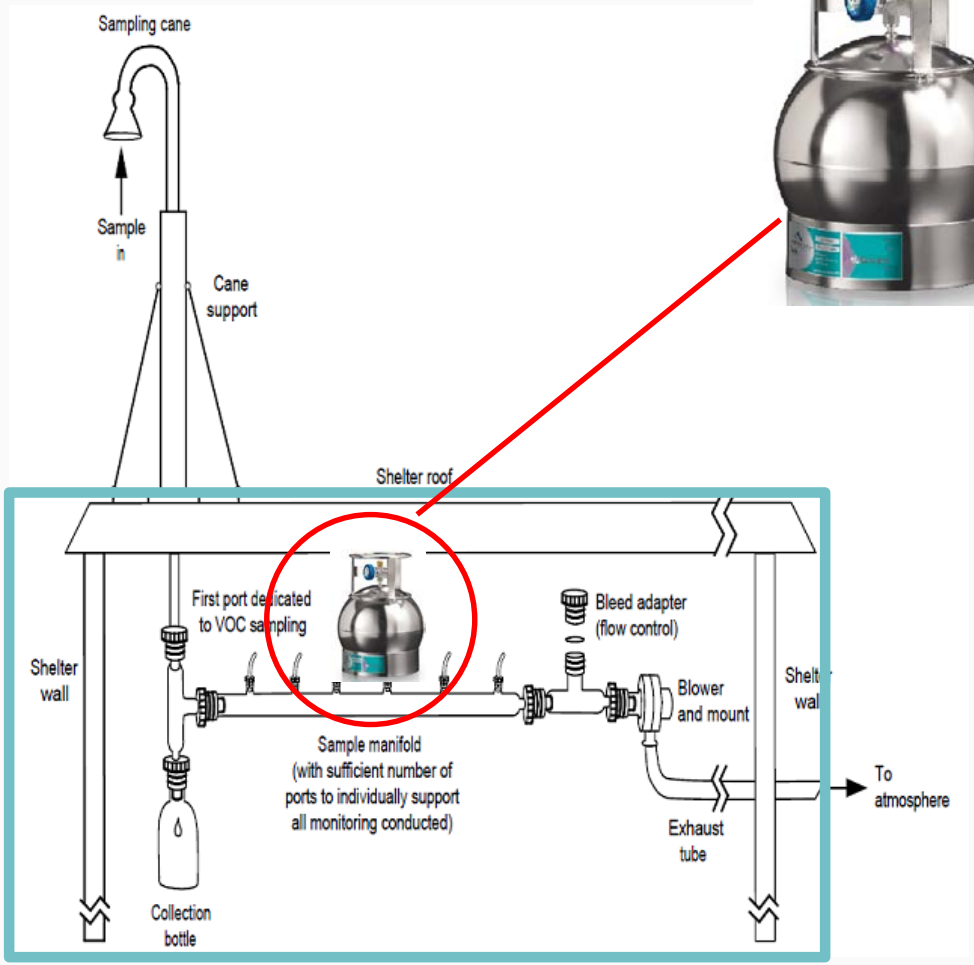
1. Summary of Results for the 2005 National-Scale Assessment: http://www.epa.gov/ttn/atw/nata2005/05pdf/sum_results.pdf

Petroleum Refinery Sector Risk & Technology Review; New Source Performance Standards

- Additional emissions control requirements
- Application of a new air monitoring method to detect fugitive emissions
- EPA set an annual average benzene concentration standard at the refinery fence line, measured using 2-week integrated samples placed around the refinery fence line perimeter.
- ***Does the proposed monitoring method compare well with current procedures?***

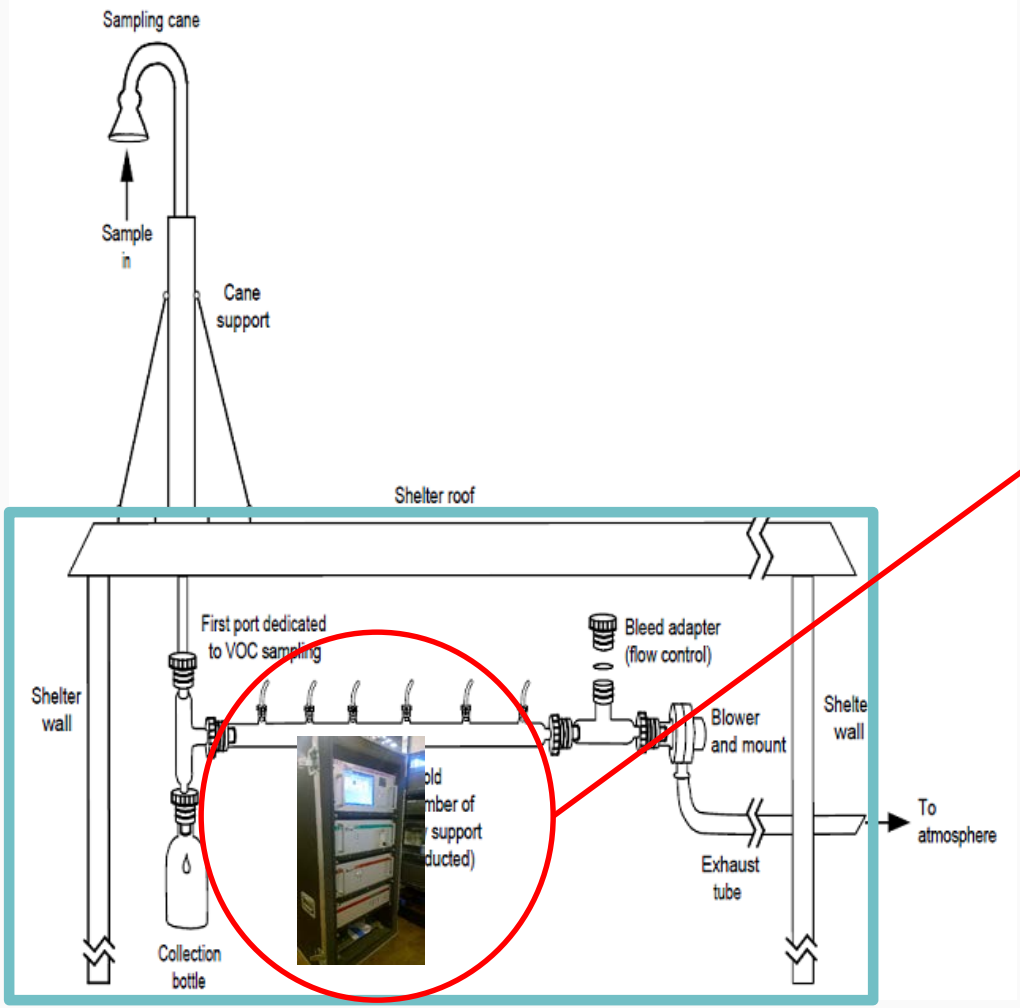
EPA's current method –
24-hr canister sample, TO-15 in lab

Used in the National Air Toxics Trends Station (NATTS) network



GC-MS

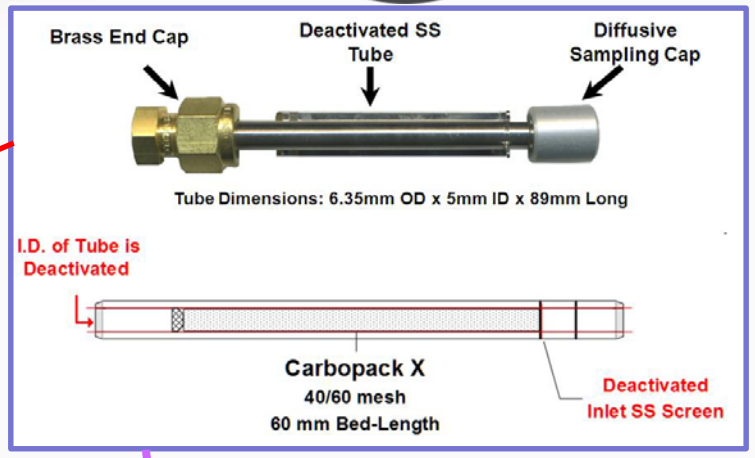
Alternative to current method – Hourly data in field via autoGC



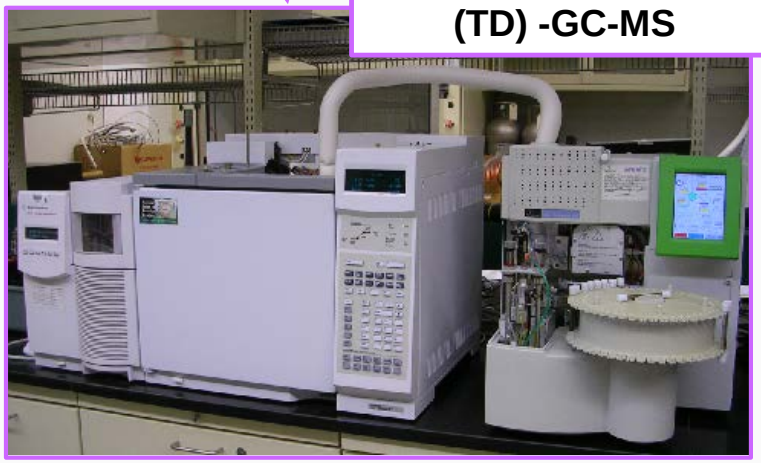
Used at Photochemical Assessment Monitoring Stations (PAMS) sites

autoGC

Proposed method – Passive tubes, collection via Modified Method 325A, analysis via Modified Method 325B



Thermal Desorption (TD) -GC-MS



This study

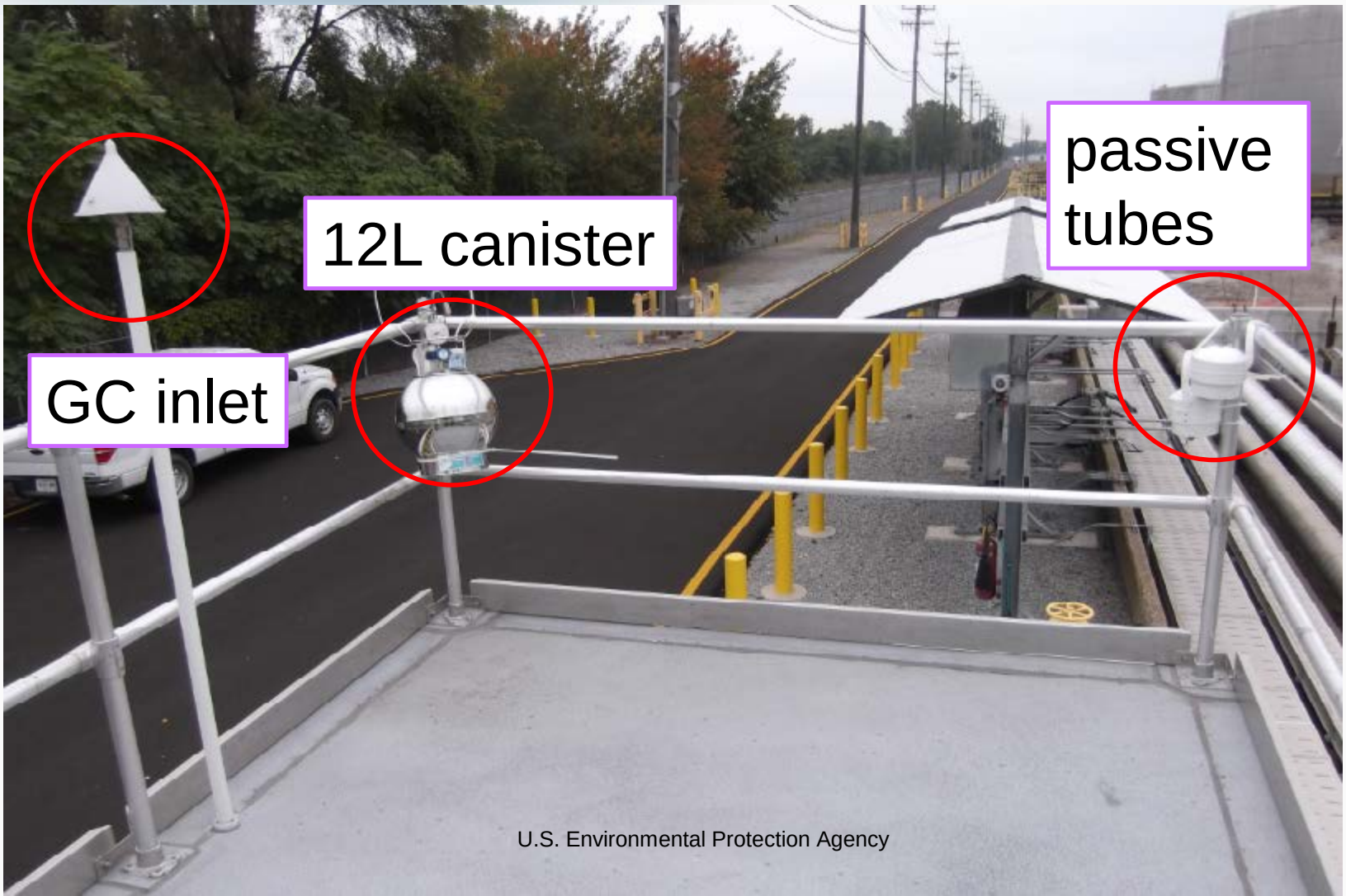
- Follow-up to an initial feasibility study led by EPA's Office of Research and Development (ORD) and Regions 3, 5, 6, & 8: "Collaborative Evaluation of a Low-Cost Volatile Organic Compounds Passive Sampling Method & Analytical Laboratory Intercomparison".
- **Our objective is to quantify the comparability of the new passive tube method to EPA's recommended method for VOC sample collection – canisters.**
- Added benefit: we received permission to piggyback sampling on an existing fenceline network of autoGC stations at an Indiana refinery.

BP Refinery, Whiting, Indiana

- Four-station fenceline network is result of 2012 agreement between refinery, regulators, & private citizen groups.
- BP committed to provide comprehensive air quality information regarding conditions at the fenceline via this public website:

http://raqis.radian.com/pls/raqis/bpw.whiting

We collected 8 sets of 1-week samples on top of GC trailers



Challenges – logistics

- Scientists not accustomed to extensive safety and security procedures at a refinery
  - field staff underwent safety training
  - fire retardant suit, reflective vest, hardhat, protective gloves, etc.
  - check in/out at each sampling location
  - everything took longer than expected
- First sampling event incomplete due to rain and risk of lightning. Several hours under “stop work” orders for outdoor activities.

Challenges – technical

- EPA-CRL provided canisters under vacuum
  - passive flow regulators on inlet, set to fill in 7 days
  - if canisters fill too quickly, they equilibrate with environment and gases diffuse in/out
- EPA-ORD provided multiple tubes each week
  - blanks & duplicates, shipped overnight in coolers
  - 2-week sampling in proposed rule
  - only 1-week sampling feasible with available canisters

Challenges – data comparison

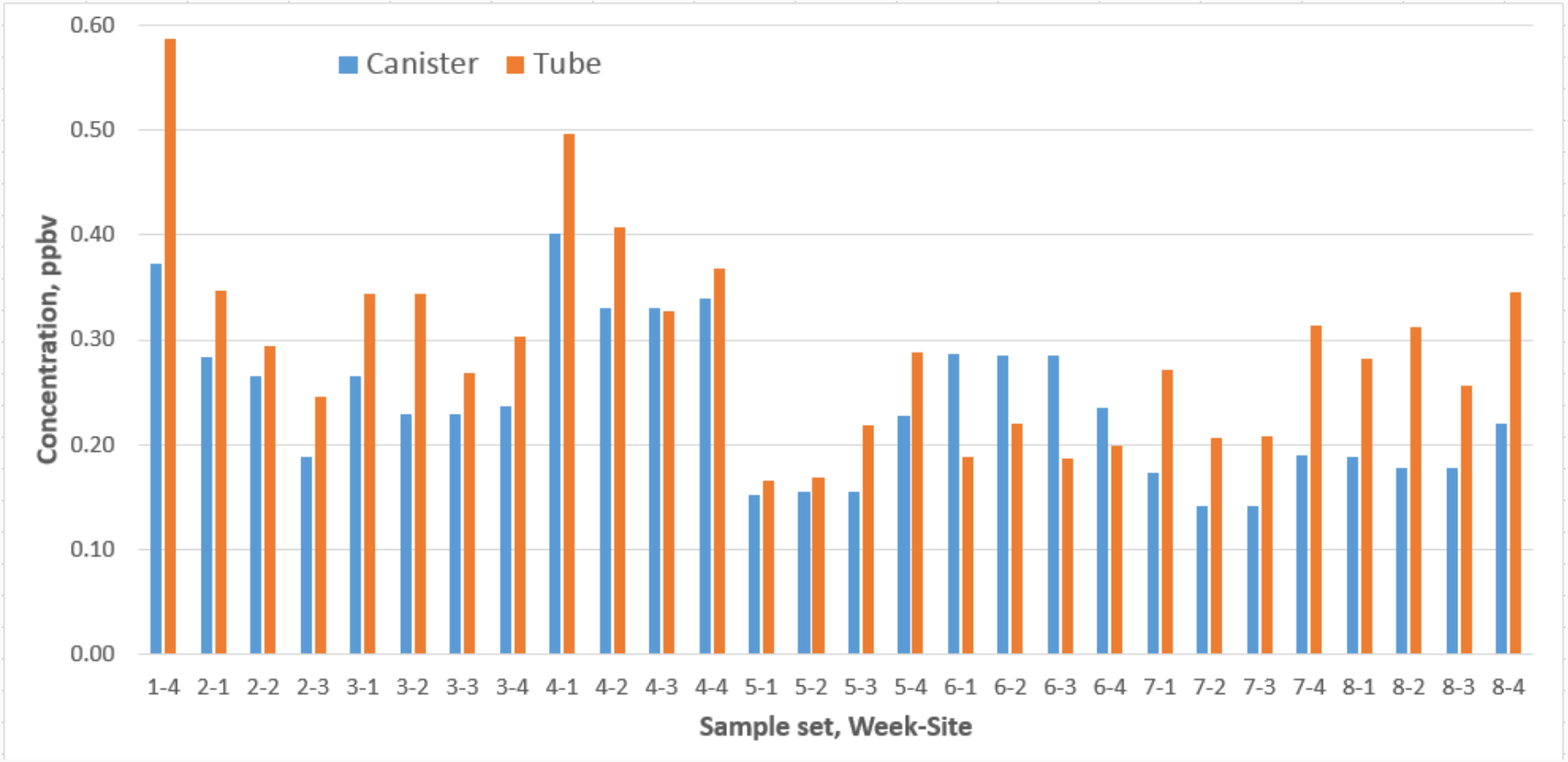
- BP posts 1-hour data on public website
  - 168 measurements per week if all reported
  - about 25% calibration events/invalid data & up to 40% nondetects
  - hourly data were averaged to match week of passives
- All participants reported different VOC list
  - CRL determined 60 analytes in canisters
  - ORD determined 9 in tubes
  - BP determines 4 via autoGC
  - only benzene and toluene on all lists

Results

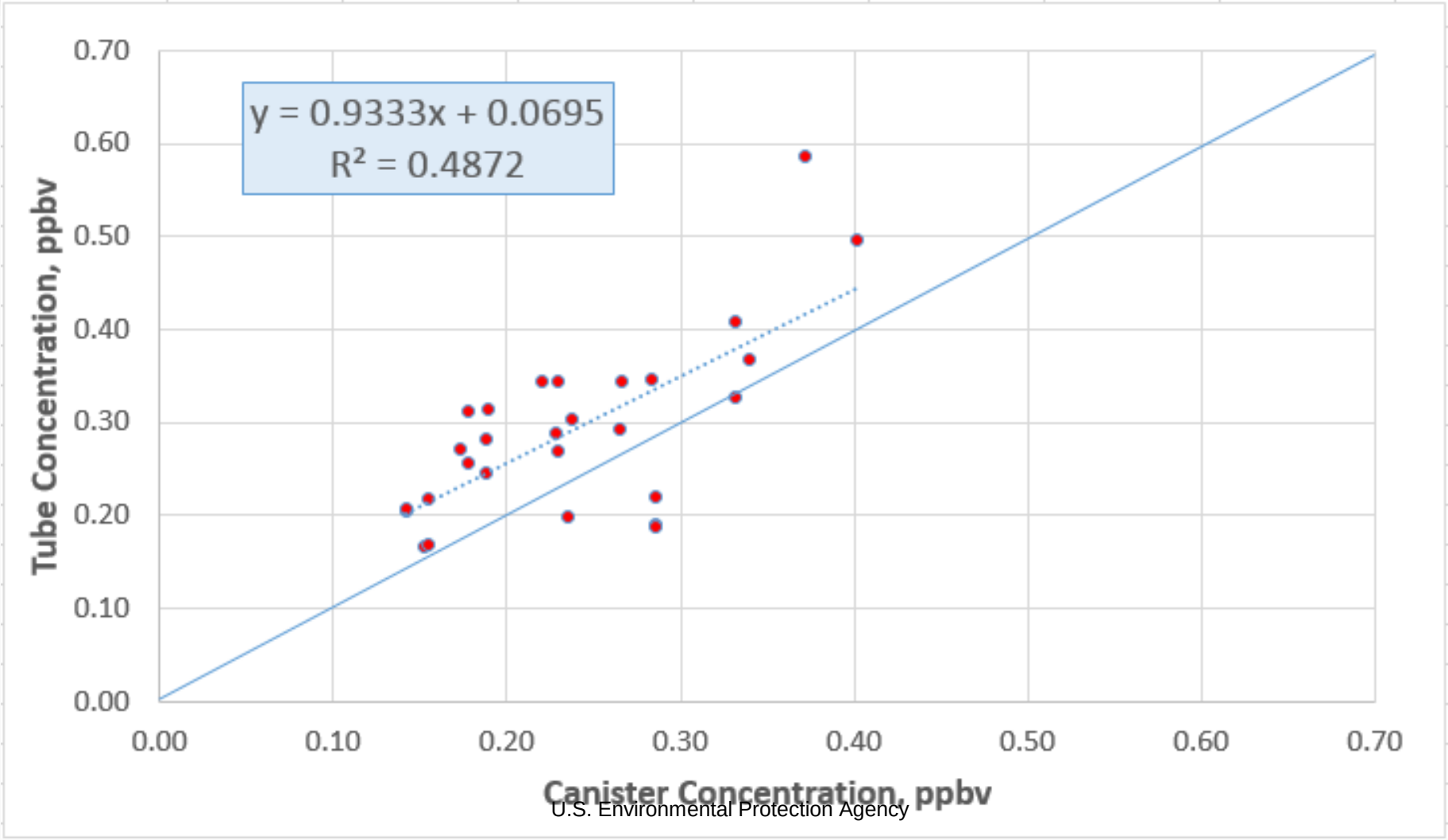
- 28 valid sets (of possible 32) 1-week paired canisters & tubes collected; analyzed at CRL and ORD, respectively
- Comparison methods
  - Plotted linear regression for full dataset
    - Correlation (R-squared), intercept, and slope
  - Calculated Relative Percent Difference (RPD) for each pair

$$\%RPD = \frac{(C_1 - C_2)}{\frac{(C_1 + C_2)}{2}} * 100\%$$

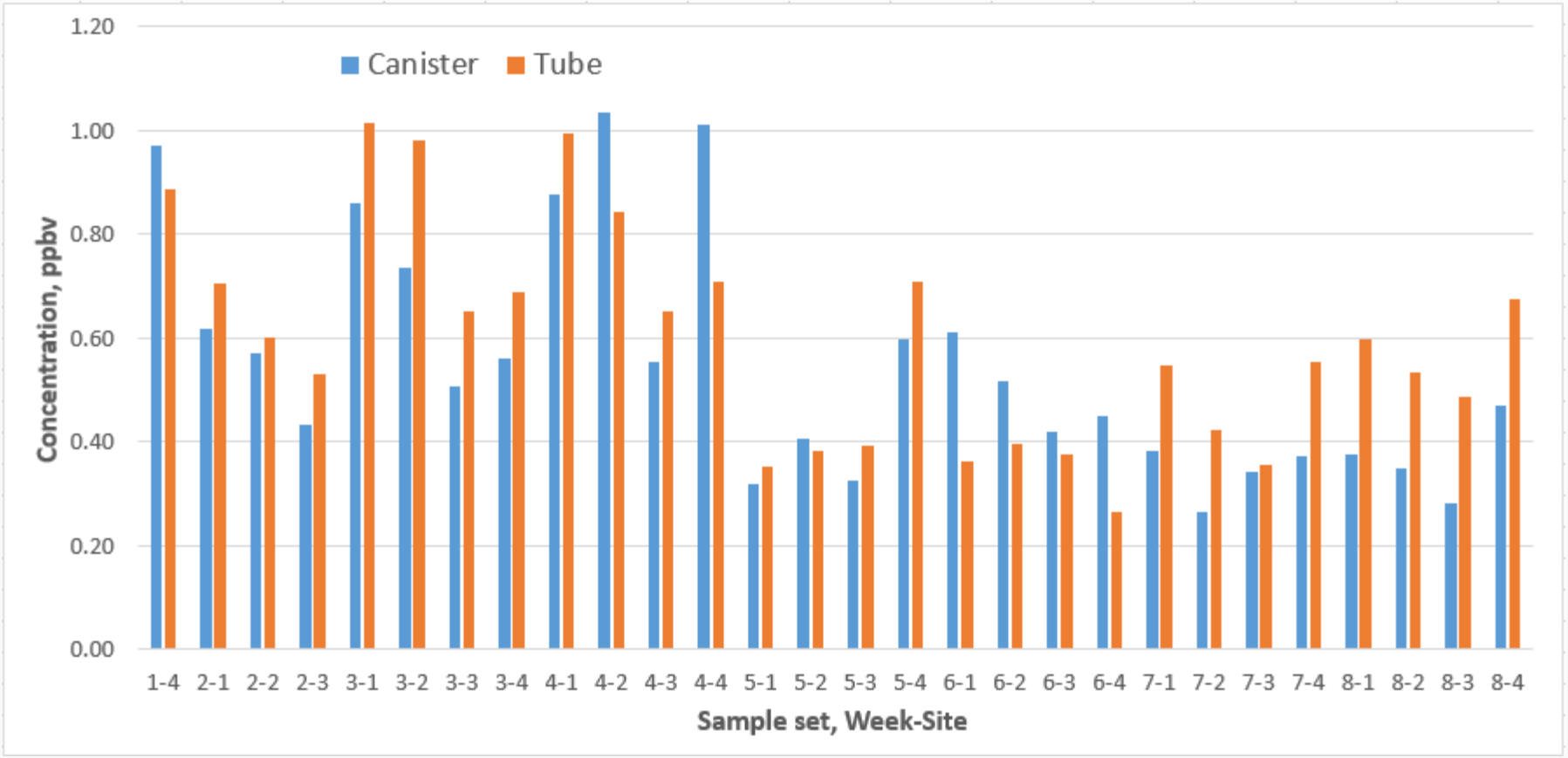
Benzene – Canister and Tube Results



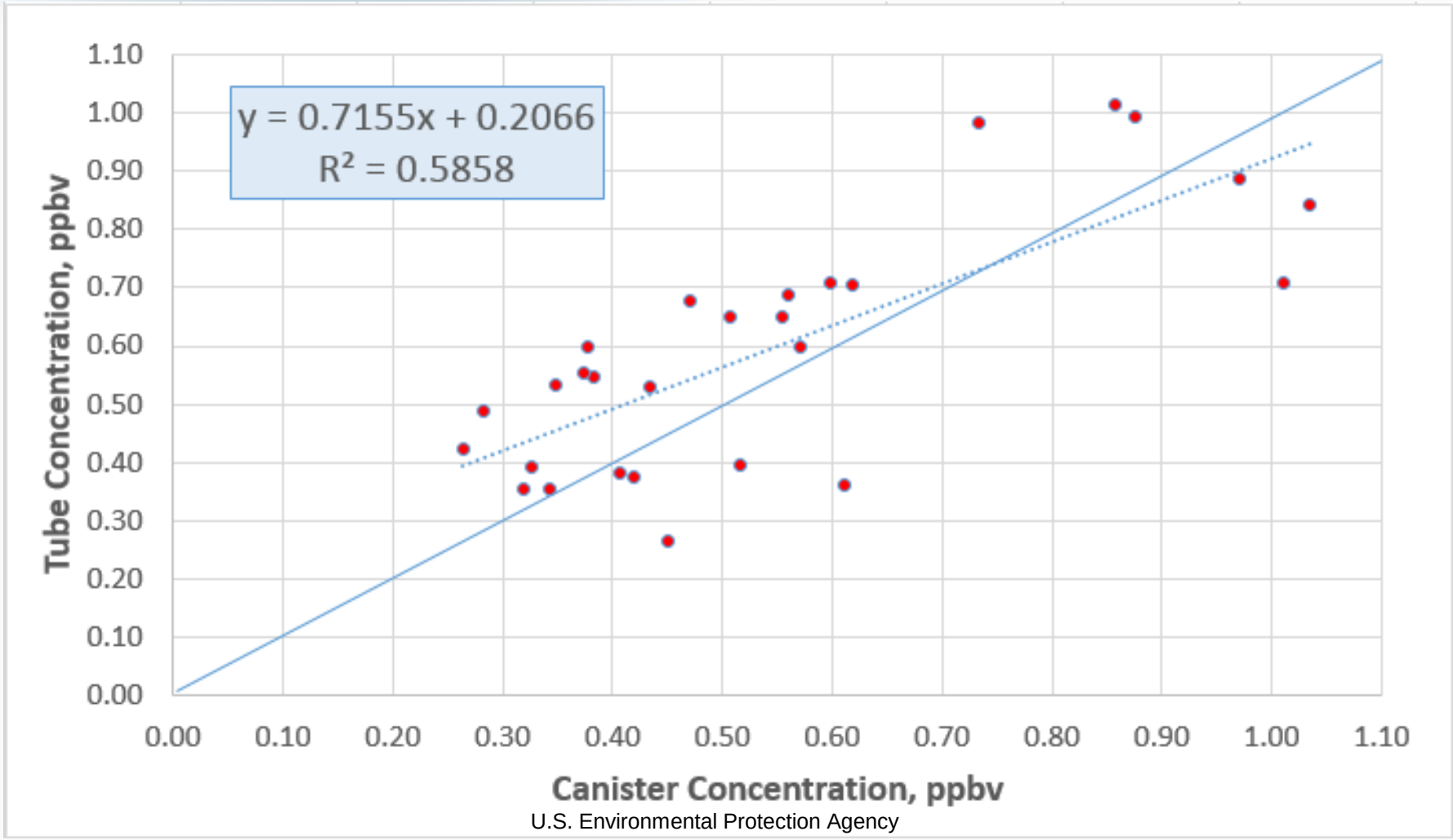
Benzene – Canister vs. Tube Regression



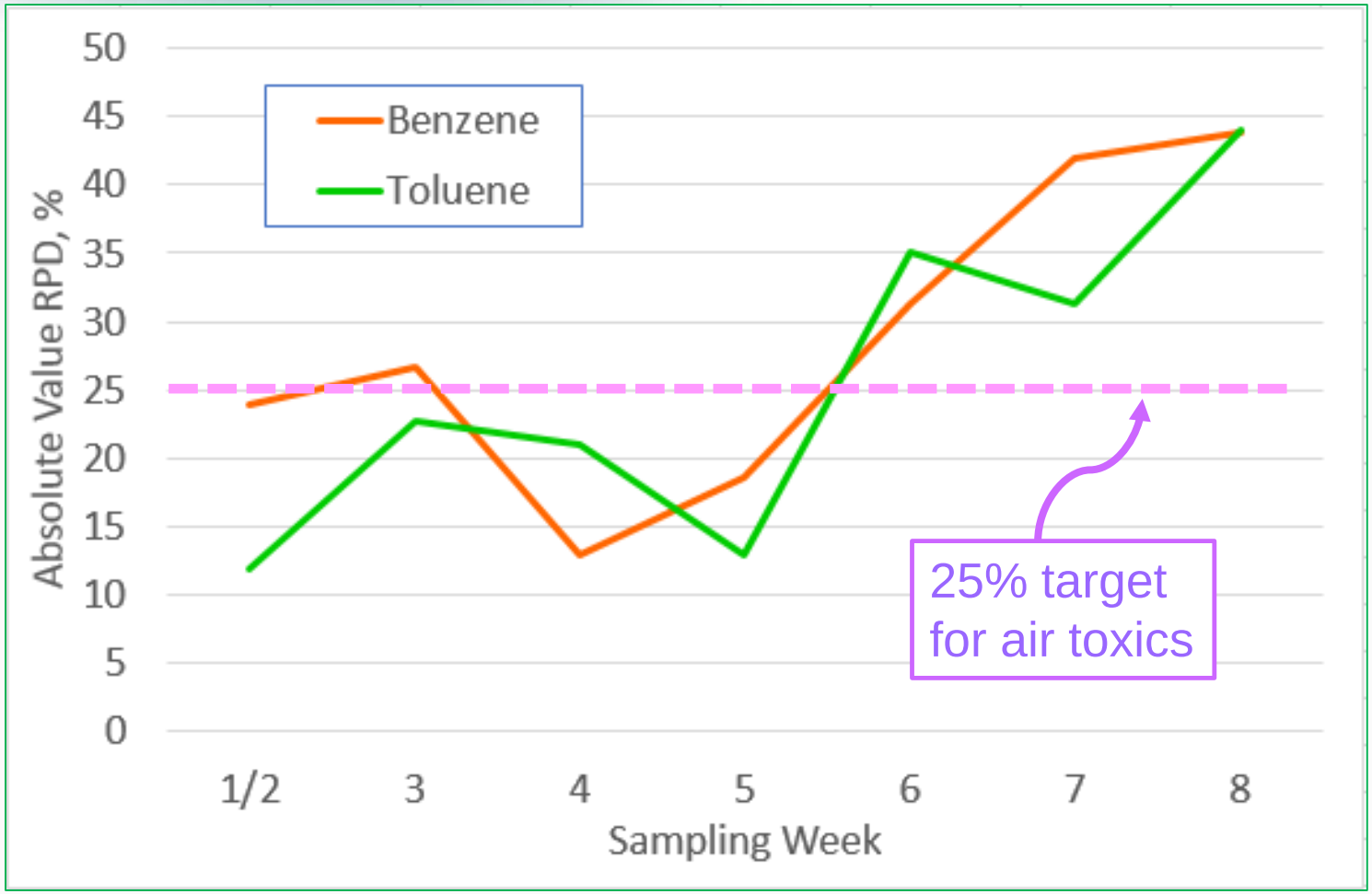
Toluene – Canister and Tube Results



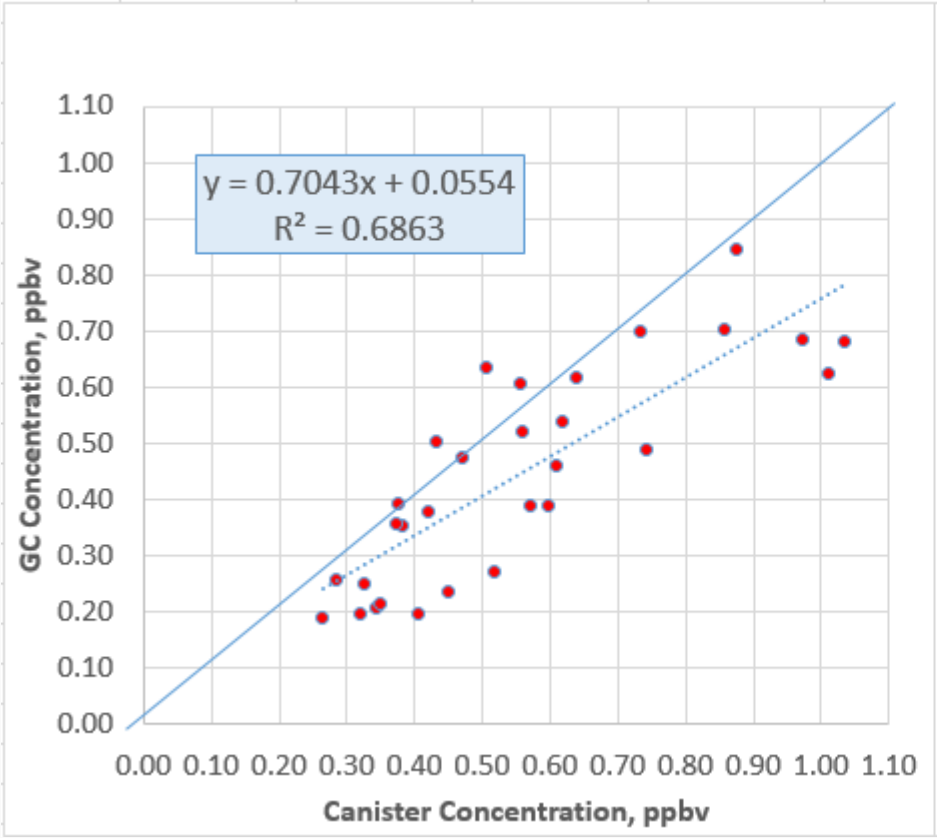
Toluene – Canister vs. Tube Regression

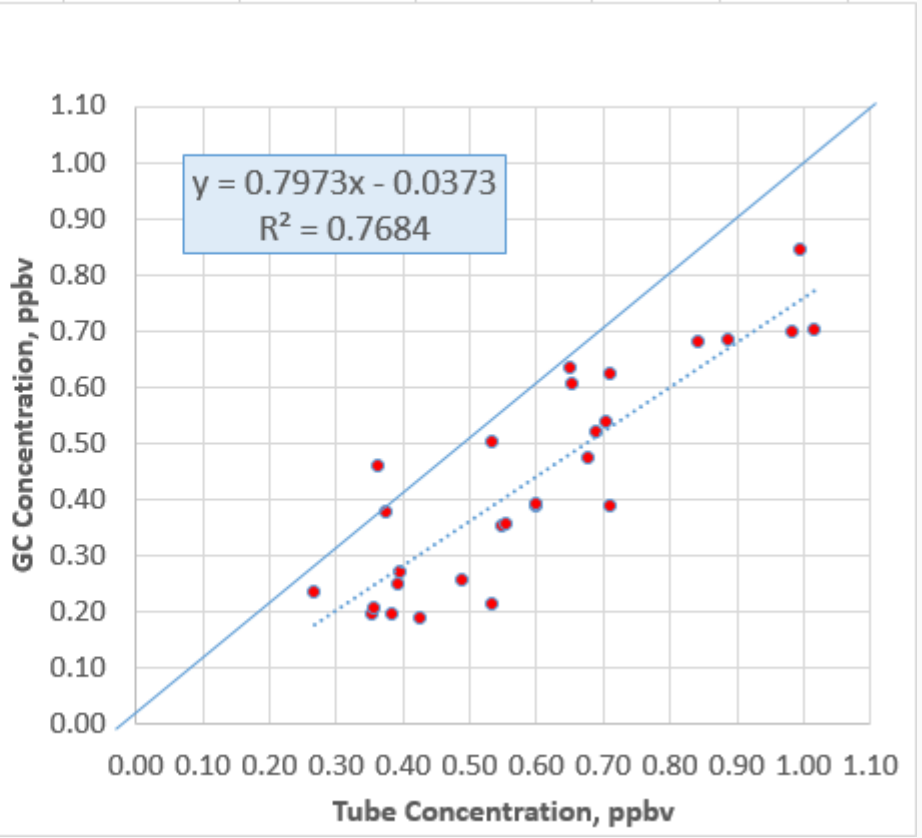


Benzene and Toluene – Canister vs. Tube RPD



Toluene – Canisters & Tubes Compared with hourly GC





Duplicate Sample Results

	Tube Results, ppbv			Canister Results, ppbv	
	Benzene	Toluene		Benzene	Toluene
Set 1	0.29	0.60			
	0.31	0.62			
Set 2	0.34	0.98		0.300	0.679
	0.34	0.95		0.230	0.472
Set 3	0.27	0.65		0.233	0.740
	0.28	0.68		0.225	0.728
Set 4	0.37	0.71		0.331	1.04
	0.38	0.71		0.331	1.03
Set 5	0.17	0.35		0.154	0.407
	0.18	0.35		0.156	0.405
Set 6	0.22	0.40		0.287	0.519
	0.23	0.41		0.284	0.514
Set 7	0.21	0.36		0.134	0.228
	0.20	0.36		0.150	0.300
Set 8	0.34	0.68		0.180	0.364
	0.37	0.79		0.175	0.333

Average Percent Difference of Duplicates

Actual Average % RPD					Absolute Value %RPD				
tubes			canisters		tubes			canisters	
benzene	toluene		benzene	toluene	benzene	toluene		benzene	toluene
-3%	-3%		3%	3%	4%	4%		7%	11%

Conclusions

- All three VOC monitoring methods compared within reasonable limits for both benzene and toluene.
- In general, the passive tube method resulted the highest concentrations and autoGC the lowest.
- More field testing is recommended to confirm that these relationships hold up during extreme summer and winter weather conditions.

Acknowledgement

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